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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Composite Ceramic Monoliths with Poly(Ester Acrylate) and Poly(Ester Acrylate)–Poly(*N*-vinylcaprolactam) Coatings

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Abstract—Polymerization of a series of oligo(ester acrylates) on the surface of ceramic monoliths was studied with the aim to prepare composite monolithic sorbents, highly porous permeable ceramic materials with polymeric coatings. A chelating organoceramic sorbent was prepared by copolymerization of an oligoester with *N*-vinylcaprolactam on a ceramic support.

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Thanks to a set of valuable properties, such as high flow rate of a mobile phase, mass-transfer efficiency, high separation efficiency, and possibility of rapid separation, purification, and analysis of mixtures of different compounds, modification of the surface of inorganic supports with polymers substantially expands the field of their application, in particular, as sorbents for chromatography of biopolymers [1–5].

This study deals with preparation of composite monolithic sorbents, highly porous permeable ceramic monoliths with poly(ester acrylate) coatings. Their preparation is based on three-dimensional polymerization of oligoester acrylates and on their copolymerization with vinyl monomers on the surface of a ceramic support with the aim to improve the selectivity and sorption characteristics. Interest in oligoesters with reactive terminal methacrylate groups as modifiers of ceramic monoliths is due to their capability to form strong three-dimensional network coatings by polymerization on a ceramic matrix and to the possibility of "transferring" the main properties of the modifier to the corresponding network polymer. This allows modification of an inorganic matrix with a polymer with the preset structure and set of properties.

EXPERIMENTAL

We used two types of permeable ceramic monoliths conventionally designated as **A** and **B**. The pore structure of support **A** consists of intercommunicating macropores of micrometer size with almost zero specific volume of sorption pores ($V_s < 0.1$ cm^3 g^{-1}) [6]. The biporous structure of support **B** consists of mesopores of the applied silica layer and of intercommunicating macropores of the ceramic framework with the specific pore volume of 0.375 cm^3 g^{-1} and specific surface area of about 100 m^2 g^{-1} [7].

To prepare oligoesters, we used freshly distilled 1,4-butanediol, ethylene glycol, diethylene glycol, and methacrylic acid. Phthalic and maleic anhydrides were used without preliminary purification. For copolymerization with oligoesters we used freshly distilled *N*-vinylcaprolactam (bp 126°C/20 mm Hg, mp 35–37°C). Oligoester methacrylates (see table) were prepared by the procedure described in [8].

Poly(ester acrylates) were applied by two procedures: (1) preliminary impregnation of monoliths with oligoester solutions for 2–60 h, followed by drying in air for 1 h to remove the solvent and polymerization in an oven at 190°C for 3 h (this is possible owing to low volatility of oligoesters); (2) polymerization in solution at 80°C in the presence of 1 wt % benzoyl peroxide for 4 h in a flask equipped with a reflux condenser. After polymerization completion, the samples were successively washed with an organic solvent (acetone or ethyl acetate), ethanol, distilled water, and again ethanol and were dried at 120°C to constant weight.

The polymer amount was estimated gravimetrically, from the weight gain of the modified sorbent, which depended on the oligoester concentration in the starting solution.

We studied polymerization of MBF-1 in the form of a 15% benzene solution at 75°C in the presence of 1 wt % (relative to the monomer) of benzoyl peroxide on the surface of ceramic support **A** and in solution (without ceramic support). The modified monoliths were withdrawn from the flask after heating for 0.25, 0.5, 1, 1.5, 2, and 3 h, kept in ethyl acetate for 1 h, and dried at 120°C to constant weight. The content of the immobilized polymers on the support ranged from 5 to 55% (Fig. 1, curve *2*). Polymerization of MBF-1 in the form of a 15% benzene solution in the presence of 1 wt % (relative to the monomer) of benzoyl peroxide at 75°C without ceramic support was performed in five separate test tubes connected to reflux condensers via ground-glass joints. After the process completion, to the resulting suspension of the cross-linked polymer we added ethyl acetate. The polymer was filtered off on glass frits, washed with ethyl acetate, and dried at 120°C to constant weight. The yield of the polymers ranged from 0 to 40% (Fig. 1, curve *1*).

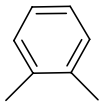
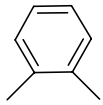
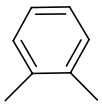
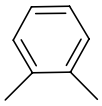
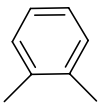
After preliminary impregnation of monoliths with oligoester solutions for 2–60 h, drying in air for 1 h to remove the solvent, thermal polymerization in an oven at 190°C for 3 h, successive washing with an organic solvent (acetone or ethyl acetate), ethanol, distilled water, and again ethanol, and final drying of the modified sorbent at 120°C to a constant weight, the content of immobilized polyesters on the ceramic support ranged from 40 to 60%.

Copolymerization of MBF-1 with *N*-vinylcaprolactam was performed in a benzene or toluene solution at 1 : 1 molar ratio of the monomers in the presence of 1 wt % (relative to sum of monomers) of benzoyl peroxide at 80 (benzene) or 110°C (toluene) for 2–5 h in a flask equipped with a reflux condenser. The monoliths modified with the copolymer were successively washed with ethyl acetate at room temperature for 24 h, ethanol, distilled water, and again ethanol, and were dried in an oven at 100–120°C to a constant weight.

The retention of copper ions by the modified ceramic sorbents was determined by the procedure described previously [9].

The IR spectra were recorded with an Avatar Nicolet FTIR spectrometer. The SEM images were taken with a TESCAN 3115 scanning electron microscope. The specific surface area of samples was measured by the BET method with an Accusorb 2100E physical adsorption analyzer (Micrometrics).

Oligoester methacrylates $CH_2=C(CH_3)COOR'O[COROOR'O]_n\cdot COC(CH_3)=CH_2$

Oligoester methacrylate	R	R'
MBF-1, $n = 1$		$(CH_2)_4$
MBF-2, $n = 2$		$(CH_2)_4$
MBF-3, $n = 3$		$(CH_2)_4$
MEF-1, $n = 1$		CH_2CH_2
MDF-1, $n = 1$		$CH_2CH_2OCH_2CH_2$–
MBM-1, $n = 1$	–CH=CH–	$(CH_2)_4$

It is known that oligoester acrylates are capable of radical polymerization via terminal or regularly arranged unsaturated groups, which ensures participation of the oligoester block of a given type in forma-

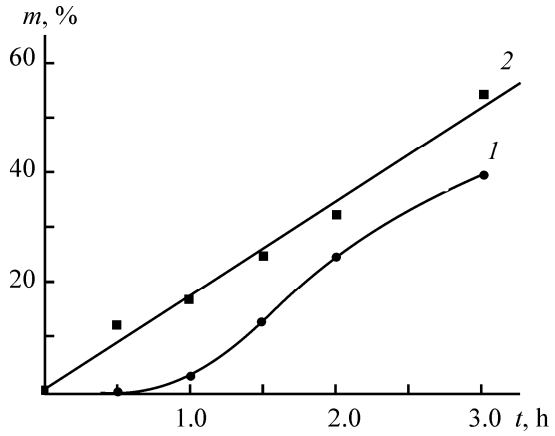


Fig. 1. Polymerization of MBF-1 (15% benzene solution with 1 wt % benzoyl peroxide) (*1*) in solution and (*2*) on a ceramic monolith at 75°C. (*m*) Polymer yield and (*t*) polymerization time.

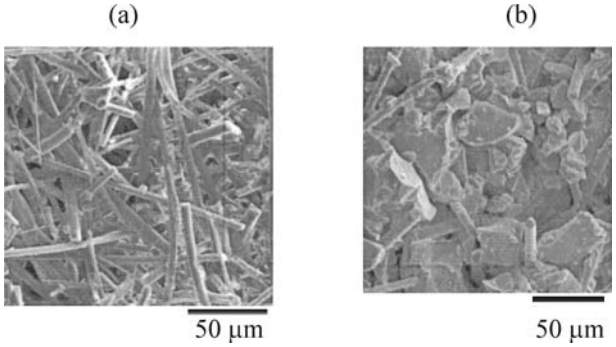


Fig. 2. SEM images of (a) unmodified ceramic monolith and (b) monolith modified with MBF-1 polyester. Magnification 1030.

tion of a three-dimensional structure of the cured polymer [8].

Studies of polymerization of MBF-1, MBF-2, and MBF-3 oligomers on ceramic supports showed that the polymers prepared from MBF-2 and MBF-3 were washed out with solvents to a considerable extent (for example, with MBF-3 the washout reached 50%). This is apparently due to weaker association of the corresponding polyesters with the support surface. Studies of polymerization of MBF-1, MEF-1, MDF-1, and MBM-1 showed that the polymerization on the surface of ceramic support **A** occurred at the highest rate and to the highest conversion with MBF-1. In this series, the immobilized polymer prepared from MBF-1 is also washed out to the smallest extent. Therefore, MBF-1 oligoester was chosen as the best compound for further studies of the polymerization and copolymerization with *N*-vinylcaprolactam.

A study of the polymerization of MBF-1 in the form of a 15% benzene solution at 75°C in the presence of 1 wt % of benzoyl peroxide in solution (Fig. 1, curve *1*) and on the surface of ceramic monolith **A** (Fig. 1, curve *2*) showed that the homopolymerization of MBF-1 in solution occurred with an induction period (0.5 h), whereas the polymer content on the ceramic in 0.5 h was 12%. The curve shapes suggest certain activating effect of the support surface on the MBF-1 polymerization, which is apparently due to specific sorption of the oligomer on the ceramic surface.

The IR spectra of MBF-1 homopolymer prepared in the bulk at 190°C and of the polymer prepared by polymerization of MBF-1 in benzene at 80°C are identical. The following characteristic absorption bands are present: the band of ester C=O group at about 1717 cm^{-1}, the bands of out-of-plane C–H bending vibrations in the aromatic ring at about 741 and 1070 cm^{-1}, weak absorption bands of C=C bonds of the aromatic ring at about 1600 cm^{-1}, C–O stretching vibrations band at about 1263 and 1124 cm^{-1}, and CH_2 stretching vibrations band at about 2965 cm^{-1}. The absorption band of the double bond at about 1635 cm^{-1} is very weak compared to the initial oligomer, which indicates that the polymerization of the oligoester on the ceramic monolith occurs to a high conversion. In the IR spectrum of the monolith modified with the poly(ester acrylate) by polymerization of MBF-1 oligoester on ceramic monolith **B** at 190°C, in contrast to MBF-1 homopolymer prepared by bulk polymerization, only the following absorption bands are present: very strong bands of ester C=O vibrations at about 1725 cm^{-1}, out-of-plane CH bending vibrations in the aromatic ring at about 795 cm^{-1}, OH stretching vibrations (silanol groups) at about 3300 cm^{-1}, and SiO_2 vibrations at 1063 cm^{-1}. The spectra of MBF-1 homopolymer and of modified monolith **A** (at relatively high polymer content) are virtually identical. In the case of modified monolith **B**, significant changes in the spectra are observed: High-frequency shift of the absorption band of C=O groups in the modified sorbent relative to MBF-1 homopolymer suggests relatively strong association of the polymer with the ceramic matrix surface, apparently, via hydrogen bonding between C=O groups and silanol groups of the support.

Electron-microscopic examination of the structure of modified monoliths (images were taken from various transverse and longitudinal sections of monoliths) showed that the distribution of the applied polymer in the monolith pore volume was fairly uniform. As example we show in Fig. 2 one of the images (Fig. 2b) in comparison with that of the unmodified monolith (Fig. 2a).

A study of pore characteristics of ceramic monolithic sorbents (water absorption, open porosity, specific pore volume, and specific surface area) showed that the specific pore volume of ceramic monoliths of type **A** became several times larger after applying poly(ester acrylate) layers, whereas for modified ceramic monolith **B** the specific pore volume, as a rule, decreased because of partial blocking of sorption pores with the polymer.

We also examined the effect of porophores on the specific pore volume of the modified monoliths.

As porophores we used various polar and nonpolar solvents: toluene, ethyl acetate, and dimethyl form-

amide (drying temperature 80, 120, 150, and 180°C). The resulting composite ceramic monoliths modified with MBF-1 polymer were kept in solutions of the above porophores (swelling) for 24 h and dried at the indicated temperatures in an oven to constant weight. The specific pore volume of ceramic monoliths **A** and **B** with the applied poly(ester acrylate) layers after keeping for 24 h in toluene and drying at 80°C to constant weight increased from 0.082 to 0.35 and from 0.213 to 0.368 $cm^3\ g^{-1}$, respectively. With an increase in the toluene evaporation temperature from 80 to 180°, the specific pore volume of modified sorbent **A** after drying to constant weight decreased from 0.35 to 0.18 $cm^3\ g^{-1}$.

With dimethylformamide and ethyl acetate as porophores, considerably smaller increase in the porosity is observed. For example, the specific pore volume of ceramic monolith **A** modified with the polyester based on MBF-1 increased from 0.052 to 0.186 and 0.112 $cm^3\ g^{-1}$ upon treatment with dimethylformamide, followed by drying at 120 and 150°C, respectively. With ethyl acetate as porophore, the pore volume after drying at 80°C increased from 0.084 to 0.181 $cm^3\ g^{-1}$. A similar increase in the specific pore volume, from 0.083 to 0.184 $cm^3\ g^{-1}$, was also observed upon heat treatment of modified monolith **A** at 180°C for 2 h.

A study of MBF-1 copolymerization on a ceramic support with vinyl monomers, in particular, with *N*-vinylcaprolactam, is of particular interest, as the latter compound is a potential chelating ligand capable of coordination binding of metal ions.

Copolymerization on a ceramic support was performed from a solution in refluxing benzene or toluene for 2 h at a monomer molar ratio of 1 : 1 and their total concentration of 5–20% in the presence of 1 wt % benzoyl peroxide. We found that the copolymerization in benzene at 80°C yielded a polymer soluble in the polymerization mixture and probably having a branched structure, whereas on a ceramic support a cross-linked polymer formed. Copolymerization in toluene at 105–110°C occurred with the formation of a cross-linked polymer in the form of a white powder precipitating from the solution from the very beginning of the polymerization. The copolymer content on the ceramic support was about 40% in both cases. The structure of the copolymer is shown below (the copolymer composition was determined from the nitrogen content according to elemental analysis, ~5.07% N).

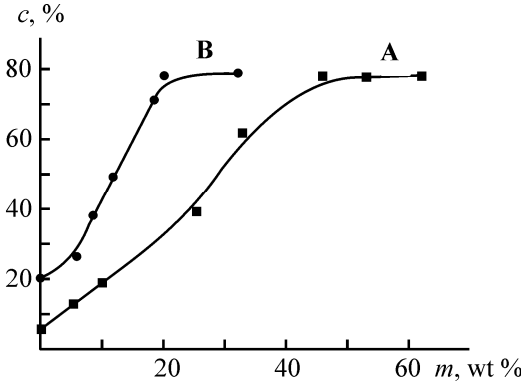
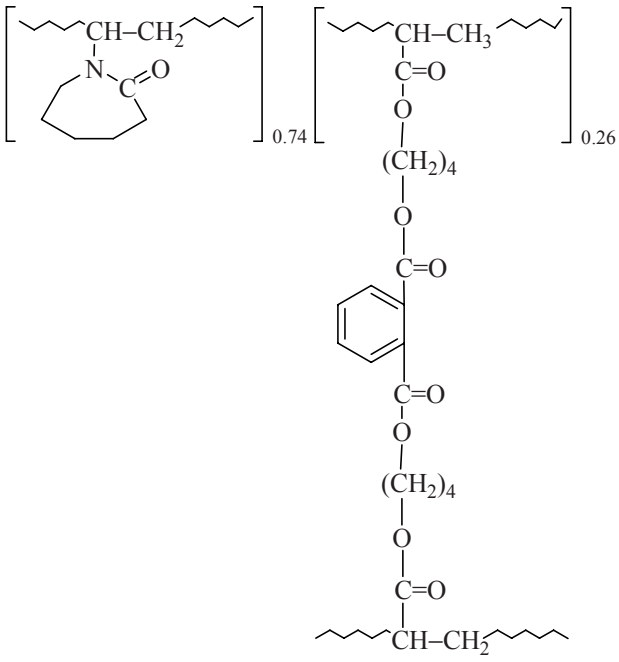


Fig. 3. Retention of Cu(II) ions with ceramic monoliths **A** and **B**, modified with the copolymer of MBF-1 with *N*-vinylcaprolactam. (*m*) Polymer content.



The IR spectrum of the ceramic monolith modified with the copolymer contains all the absorption bands present in the spectrum of the monolith modified with poly(ester acrylate) based on MBF-1: 1065 (SiO_2), 1716 (C=O), 740 and 1070 (benzene ring), 1262 and 1125 (C–O), 2967 cm^{-1} (CH_2), and also all the absorption bands characteristic of amide group: 1633, 3290–3330, 1540 cm^{-1}. The absorption bands of residual $CH{=}CH_2$ groups that have not been involved in polymerization (1600 cm^{-1}) are weak compared to the starting oligomer.

Sorbents based on ceramic monoliths **A** and **B** and on copolymer of MBF-1 with *N*-vinylcaprolactam were tested for the retention of copper ions from a 1 M

copper sulfate solution. The retention of Cu^{2+} ions as a function of the polymer content on the support is plotted in Fig. 3. As can be seen, at 50% content of the copolymer on ceramic monolith A the retention of copper ions is 78%, whereas 79% retention of copper ions with ceramic **B** is attained at a considerably lower polymer content on the sorbent. It should be noted that retention of copper ions with monoliths **A** and **B** modified with MBF-1 homopolymer does not exceed 30%.

Our results show that, with ceramic **A** containing no porous silica layers, the content of the cross-linked polymer in the framework of the ceramic monolith should be significant (>40%). The use of porophores results in formation of a porous structure of the polymer phase. In the case of ceramic **B** with applied silica layers, to improve the structure of sorption pores, the polymer should be applied in a considerably smaller amount (10–20%); the use of toluene as a porophore probably leads to the formation of secondary pores in polymer layers.

CONCLUSIONS

(1) Radical polymerization of oligo(ester methacrylates) on ceramic monoliths, performed after preliminary impregnation of monoliths with oligoester solutions, or polymerization on supports in solution at 80°C in the presence of benzoyl peroxide yields poly(ester acrylate) coatings with strong association of the polymer with the ceramic support and uniform distribution of the polymeric coating in the bulk of the porous monolith.

(2) The use of porophores (toluene, ethyl acetate, dimethylformamide) results in an increase in the pore volume of the modified sorbent. A chelating organoceramic sorbent retaining up to 80% of copper(II) ions was prepared by copolymerization of the oligoester with *N*-vinylcaprolactam.

(3) With the ceramics with applied silica layers, the required sorption capacity is reached by applying a polymer in a smaller (by a factor of 2–3) amount than without the silica layer.

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